

PATENT APPLICATION
Mo5457
MD-96-52-PU

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GROUP 1700

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF

KARL W. HAIDER ET AL

SERIAL NUMBER: 09/474,114

FILED: DECEMBER 29, 1999

TITLE: HYDROPHOBIC LIGHT STABLE
POLYURETHANE ELASTOMER
WITH IMPROVED MECHANICAL
PROPERTIES

GROUP NO.: 1711

EXAMINER: R. A. SERGENT

DECLARATION UNDER 37 CFR 1.132

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

Sir:

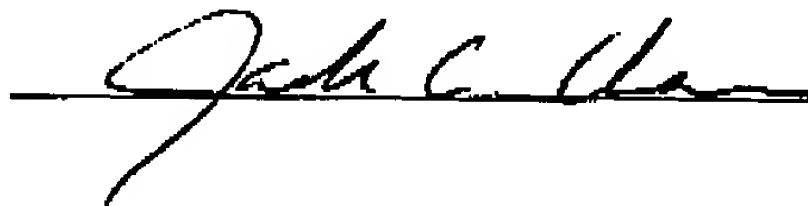
I, Jack C. Chan, of Mission Viejo, California declare as follows:

1. I studied chemistry at the University of Texas at Austin and obtained a Ph.D. degree in 1994.
2. I am employed by Bayer Polymers LLC in Irvine, California as Technical Marketing Specialist.
3. I am one of the named inventors of the above-identified United States patent application.
4. I performed or supervised the experiments described in the above-identified United States patent application.

5. I further declare that I am one of the named inventors of United States Patent Number 6,166,166, and I unambiguously declare that I, along with my co-inventors, conceived of or invented the subject matter disclosed therein.

6. The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the above-identified United States patent application or any patent issuing therefrom.

Signed at Irvine, CA, this 17th day of June, 2003.



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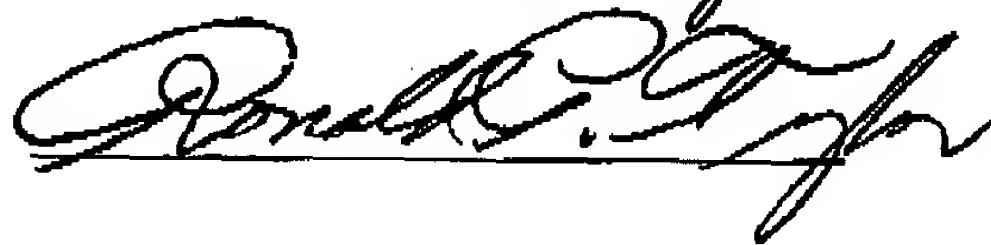
I, Ronald P. Taylor, of Moon Township, Pennsylvania, declare as follows:

1. I studied chemistry at the University of Illinois and obtained a Ph.D. degree in 1972.
2. I am employed by Bayer Polymers LLC in Pittsburgh, Pennsylvania as Head of Intellectual Property Management, BPO Business Development.
3. I am one of the named inventors of the above-identified United States patent application.
4. I performed or supervised the experiments described in the above-identified United States patent application.

5. I further declare that I am one of the named inventors of United States Patent Number 6,166,166, and I unequivocally declare that I, along with my co-inventors, conceived of or invented the subject matter disclosed therein.

6. The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the above-identified United States patent application or any patent issuing therefrom.

Signed at PITTSBURGH, PA., this 17th day of June, 2003.



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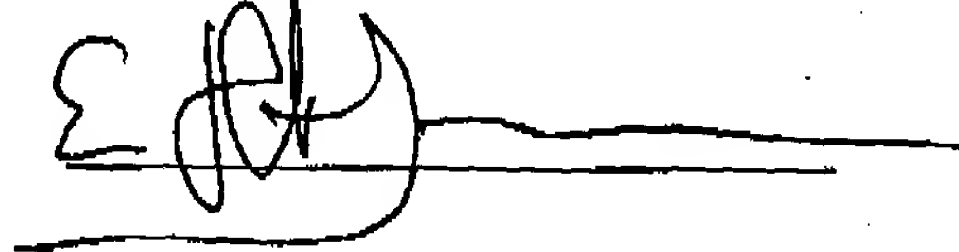
I, E. Haakan Jonsson, of Cranberry Township, Pennsylvania, declare as follows:

1. I studied polymer technology at The Royal Institute of Technology, Stockholm, Sweden and obtained a Ph.D. degree in 1991.
2. I am employed by Bayer Polymers LLC in Pittsburgh, Pennsylvania, as Vice President, Innovation Americas.
3. I am one of the named inventors of the above-identified United States patent application.
4. I performed or supervised the experiments described in the above-identified United States patent application.

5. I further declare that I am one of the named inventors of United States Patent Number 6,166,166, and I unequivocally declare that I, along with my co-inventors, conceived of or invented the subject matter disclosed therein.

6. The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the above-identified United States patent application or any patent issuing therefrom.

Signed at Pittsburgh, this 17th day of June, 2003.



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Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

Sir:

I, Uli W. Franz, of Duesseldorf, Germany, declare as follows:

1. I studied chemistry at the Technical University Munich, Germany and obtained a Ph.D. degree in 1994.

2. I am employed by Bayer AG in Krefeld, Germany, as BPO-GO-PCS-GPM, Global Industry Manager.

3. I am one of the named inventors of the above-identified United States patent application.

4. I performed or supervised the experiments described in the above-identified United States patent application.

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5. I further declare that I am one of the named inventors of United States Patent Number 6,166,166, and I unequivocally declare that I, along with my co-inventors, conceived of or invented the subject matter disclosed therein.

6. The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the above-identified United States patent application or any patent issuing therefrom.

Signed at Krefeld, Germany, this 23 day of June, 2003.

M. Franz

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- 2 -

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TECHNOLOGY

VOLUME 6

of these polyethers over the period of 1961 to 1964 was 40% per year; a 10% yearly increase is expected from 1964 through 1970 (110).

Although polyether-based flexible foams have accounted for the major portion of polyurethan production, rigid urethan foams based on various propylene oxide adducts are expected to rise fast and by 1968 should outstrip the flexible urethans (35). The use of propylene oxide in the manufacture of nonionic surfactants is expected to rise steadily through 1968, but the oil-demulsifying market for poly(oxypropylene) glycol is not expected to change much in the next five years. The consumption of poly(oxypropylene) glycols for hydraulic fluids and lubricants is also expected to increase.

Specifications and Test Methods

One of the first polyether polyols derived from propylene oxide that was produced in volume and that had suitable quality for the production of polyurethans was a poly(oxypropylene) glycol with a molecular weight of 2000. Specifications and some typical properties established by the American Society for Testing and Materials for "Urethan Grade" poly(oxypropylene) glycol with a molecular weight of 2000 are shown in Table 18. For specifications and properties of other commercially available polyethers derived from propylene oxide, the suppliers' technical bulletins should be consulted.

Table 18. Specifications and Typical Properties for "Urethan Grade" Poly(oxypropylene) Glycol of 2000 Molecular Weight (117)

<i>Specifications</i>	
hydroxyl number	54.5-57.5
acid number, max	0.1
modified APHA color, max	50
unsaturation, max, meq/g	0.04
water, max, %	0.1
sodium and potassium, max, ppm	10
<i>Typical properties</i>	
specific gravity at 25/25°C	1.003-1.006
n_D^{25}	1.448-1.449
copper, %	<0.002
manganese, %	<0.001
flash point, Cleveland open cup, °F	450

The commercially available polyethers derived from propylene oxide are shipped in 4,000, 8,000, and 10,000 gallon tankcars and 55-gallon steel drums. Polyethers derived from propylene oxide are stable, noncorrosive, high-flash-point products that can be stored in carbon steel tanks. However, if traces of iron are objectionable in the projected end use, a steel tank protected with a baked phenolic coating can be employed. Tanks containing polyether polyols should be blanketed with dry air or nitrogen to minimize moisture pickup during storage.

Test Methods. The American Society for Testing and Materials (111) has reported test methods for the following properties of polyether polyols: hydroxyl number, unsaturation, acid number, alkalinity number, total basicity, water content, sodium and potassium content, viscosity, color, specific gravity, and suspended matter.

Regardless of whether a polyether derived from propylene oxide is used as an intermediate in the manufacture of polyurethans, a surface-active agent, a lubricant,

or a hydraulic fluid, the hydroxyl number is of special importance because of its relationship to the hydroxyl equivalent weight of the polyether (see eq. 14). Thus, if the

$$\text{hydroxyl equivalent weight} = \frac{(56.1)(1000)}{\text{hydroxyl number}} \quad (14)$$

hydroxyl functionality of a compound produced by reacting an alkylene oxide with an active-hydrogen compound is known, the molecular weight may be calculated from the hydroxyl number.

Specific test methods for determination of flash point, fire point, pour point, and foaming characteristics are available for polyethers used as lubricants or hydraulic fluids (112). Propylene oxide derivatives used as surface-active agents are characterized by their cloud point (measure of water solubility) and tests which measure surface-active properties such as wetting, foaming, and detergent capabilities.

Health and Safety Factors

Polyethers derived from propylene oxide are very low in acute oral toxicity and are not appreciably irritating either to the eyes or skin. Because the polyethers derived from propylene oxide are essentially nontoxic, stable, noncorrosive, and have high flash points, no special safety precautions are normally required.

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find applications as automotive cushions, carpet underlay, furniture, seating, and bedding.

Rigid foams are based primarily on polyfunctional, low molecular weight alcohols and amines. Most global applications conventionally use polymeric isocyanates, TDI, or an undistilled grade of mixed TDI isomers. TDI prepolymers which have hydroxyl and isocyanate groups have been marketed as a low vapor pressure alternative to undistilled TDI. Density reduction is effected via the addition of chlorofluorocarbons, low molecular weight alkanes, or via the *in situ* generation of carbon dioxide. The resultant closed cell foams find applications as insulators in construction, appliance, transportation, pipeline, and tank end uses.

Similarly, polyisocyanurate (PIR) rigid foams are based on PMDI and polyester or polyether polyols (and blends thereof). The cross-link density, aromatic content, cell wall thickness, and polymer distribution are known to have a pronounced effect on the overall performance of the foam. Polyisocyanurate foams are used extensively in industrial applications having service temperature ranges from -200 to 150°C . These foams are known to provide efficient thermal insulation characteristics and structural integrity to a variety of composite applications. Apart from roofing and sheathing, PIR foams are used in garage doors, building panels, and foaming applications. They can also be supplied in the form of boardstock for fabrication into sheets, pipe covering, and other shapes.

Adhesives and coatings formulations utilize both MDI and TDI along with a variety of polyether and polyester polyols. The largest segment of the business is the one-part or moisture-cured approach, which is heavily reliant on prepolymers. Optionally, blocked isocyanate technology may be used to provide systems having an extremely long shelf life. Suitable blocking agents include phenols, diethyl malonate [105-53-3], acetone oxime [127-06-0], and ϵ -caprolactam [105-60-2]. Typical applications include flexible film packaging and wood furniture assembly. Two-part reactive adhesives employ a mixture of pure isocyanates and prepolymers and are primarily used for industrial product assembly and commercial construction.

Elastomers are segmented block copolymers. They employ a mixture of pure MDI-based isocyanates and prepolymers. The hard blocks consist of high melting MDI-glycol units which aggregate via hydrogen bonding to provide a high degree of virtual cross-linking. Suitable glycols include ethylene glycol [107-21-1], butanediols, and hexanediols. The soft block consists of high molecular weight poly(alkylene oxide) polyols. These materials are noted for their resiliency, abrasion resistance, solvent resistance, and the high level of tensile, tear, and elongation performance. Applications include shoe soles, wheels, rollers, belts, gaskets, and thermoplastic polyurethanes. Methylenediphenyl diisocyanate (MDI) is used extensively in the production of Spandex fibers. Spandex is used in foundation garments and swimwear (see FIBERS, ELASTOMERIC). Typical demand for various applications is presented in Table 7.

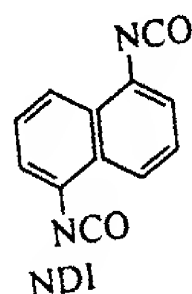
Aliphatic Isocyanates. Aliphatic diisocyanates have traditionally commanded a premium price because the aliphatic amine precursors are more expensive than aromatic diamines. They are most commonly used in applica-

[Ref. p. 39]

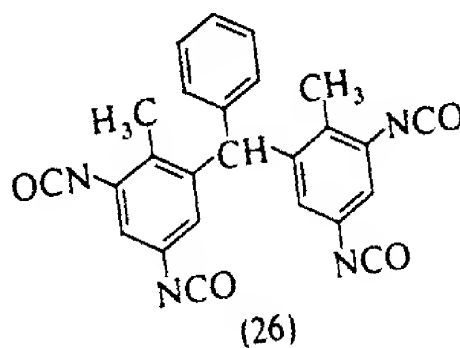
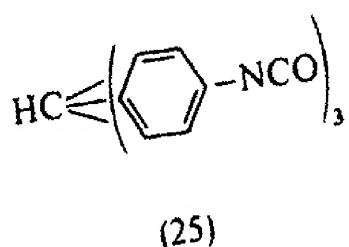
The pure 4,4'-MDI isomer is preferably used for the manufacturing of high performance polyurethane elastomers. The mixtures consisting of higher three-ring and poly-ring-containing products generally are called polymeric MDI. This book uses this nomenclature too, although these products are not actually polymers but rather oligomeric MDI types. Polymeric MDI is the basis for most rigid foam formulations. On the other hand, certain MDI types, specifically those which contain higher 2,4'-isomer contents, can also be used for flexible polyurethane foam.

Further development in the manufacturing processes for MDA and MDI was a necessity because of the ever increasing requirements for more specific MDI types. More recently, extraction processes [38] appear to be most efficient with respect to product flexibility and ecological advantages. The extraction process permits the recycling of the hydrogen chloride which is used as the catalyst for the condensation of aniline with formaldehyde. Thus, in the extraction process the neutralization of the hydrochloric acid and the subsequent disposal of the salt are eliminated.

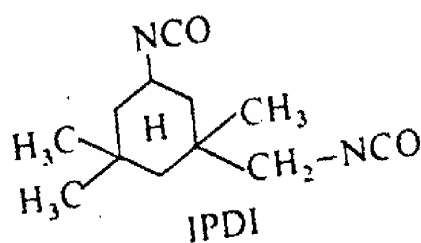
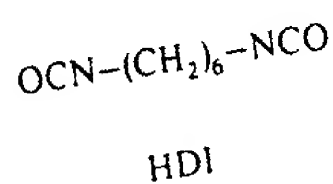
Naphthalene-1,5-diisocyanate (NDI) is a specialty among the aromatic isocyanates. It is specifically used for the manufacture of high performance cast elastomers (Vulkollan®).



Typical examples of higher functional basic polyisocyanates are 4,4',4''-triisocyanatotriphenylmethane (25) and the tetraisocyanate (26). These products are used for adhesive applications.



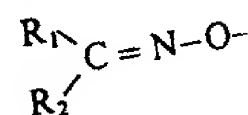
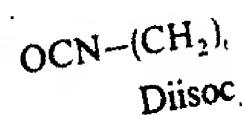
The most important basic products from the aliphatic and cycloaliphatic series are 1,6-hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) (isocyanatomethyl-3,5,5-trimethyl-cyclohexane).



The two NCO groups of the isophorone diisocyanate have different reactivity. And there are also the hydrogenated (reduced) MDI types. These aliphatic diisocyanates are used as such or in a modified form, mainly for coatings. Other aliphatic diisocyanates, such as lysine ester diisocyanate or 1,4-bis-isocyanatomethyl benzene and the analogous cyclohexane compound, have remained of minor technical importance.

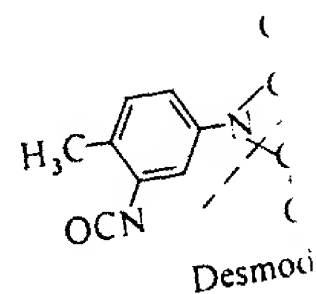
[Ref. p. 39]

As already mentioned the basic isocyanate modification could be functionality, or reaction. The modification can be in such a manner as carbodiimide, biure, or special catalysts which are possible and can be combined with oligomeric urethane isocyanates are produced. The capping or blocking of isocyanates. In this case a weak bond. The isocya



The reactive isocyanate group can react in a manner with OH- or NH compounds for the block compounds, such as ethyl acetate [39, 40]. Blocked isocyanate [41].

Dimerized isocyanates can be formed with phosphine catalysts [42] thermal treatment, and also without the liberation of importance (e.g., the dimer).



mainly as curing agents for

As a further step toward simplification of the cast technique, as well as improved industrial hygiene, the one component cast systems should be mentioned. Their technical perfection and material properties attainable at this time are not suitable for all requirements, which explain their limited scope. Generally they are ϵ -caprolactam blocked NCO prepolymers, primarily based on TDI-polyester, with aromatic diamines. Processing is extremely simple. It requires only heating the filled mold for several hours, during which the thermally labile caprolactam complex slowly dissociates. The NCO groups are released and react with the dissolved crosslinker to form thermally stable urea groups. The ϵ -caprolactam which is released remains in the casting as a contaminant and may be a cause of the reduced physical property values obtained with these elastomers. It is possible that the polar caprolactam is associated with the urea linkage, which inhibits formation of the pseudo-crystalline hard segments, and acts as an internal lubricant between the polymer chains.

[Ref. p. 447]

8.1.1.1 Raw materials

Diisocyanates

As with all polyurethane application areas of technical importance, only a limited number of diisocyanate types are used for the production of cast elastomers. Most products are based on 4,4'-diisocyanatodiphenylmethane (MDI) or 2,4- or 2,6-toluene-diisocyanate. These basic components are used in pure, modified or prepolymer form.

In the hot cure systems, monomeric diphenylmethane diisocyanate of predominately 4,4'-isomer content finds widespread use. By increasing the content of the 2,4'-isomer, the melting point of the 4,4'-isomer (ca. 38°C) can be lowered. This leads to processing advantages, primarily in the cold cure systems. The differing reactivity of the two NCO groups in the isocyanate molecule and the altered steric structure in the polymer can be utilized to obtain special effects.

Modification of the MDI, for example, by partial carbodiimide formation or by reacting a portion of the NCO groups with polyol to form semi-prepolymers, serves to lower the melting point without changing the isomer content. Also, mixing with small amounts of polymeric MDI has the same effect.

Direct use of monomeric TDI for production of cast elastomers is relatively infrequent. In addition to industrial hygiene reasons, its use is conditional upon the differing reactivity of the NCO groups in the molecule. In nearly all cast systems based on TDI, the isocyanate comes in prepolymer form for use. A defined ratio of 2,4- and 2,6-isomer content may be favored, depending on the types of the other components.

The oldest high property, hot cure casting system is based on 1,5-naphthalenediisocyanate (NDI). The aliphatic diisocyanates, 1,6-diisocyanatohexane (HDI) and 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI) and also the aromatic 4,4'-diisocyanate-3,3'-dimethylbiphenyl (TODI) only find application in very special cast systems. (Detailed descriptions of the isocyanates and their environmental concerns are found in Chapter 3; for a list of product names of the more important raw materials, see Chapter 15).

If storage precautions are observed, such as proper conditions of temperature and time (especially for MDI systems) and protection from moisture (necessary for all isocyanates and prepolymers), then most products of this type require no special preparation before use. Only higher viscosity types, such as NCO prepolymers, should be vacuum degassed at elevated temperature immediately prior to use in order to produce bubble free castings.

Polyols

Polyesters and polyethers are mainly used as the polyol component in the hot cure systems. Most polyesters are linear, hydroxyl terminated and between 1000 and 3000 molecular weight, generally around 2000. They are either comprised of one or two glycols with adipic acid, or

[Ref. p. 447]

made by polymerizing the polyadipates, influencing (strength, low temperature resistance) of hydrolytic attack. Frequently, poly(tetrahydrofuran) is used for its resistance. Only by using a degree of hydrolytic resistance. Poly(oxypropylene-glycol) molecular weights between 1000 and 2000 are used exclusively in the cold cure systems as the previously mentioned hydroxyl groups, such as the previously mentioned list of the most important polyols. All polyols, and polyols storage. Therefore, it is essential that they be stored in a dry, inert atmosphere. Generally the polyols are dissolved in air.

Crosslinkers

As was mentioned earlier, crosslinkers are added separately to the cast systems. This depends on the reaction mechanism. TDI-based cast systems use 4,4'-methylenebis(chloroaniline) (MOC) as crosslinker to reduce the reactivity. Developmental efforts are made to meet the requirements of the end users. The concerns of the end users are the hydroxyl groups, which do not react with the isocyanate groups. Many materials are difficult to prepare, but have recently attained high properties [4]. Also, 1,3-propanediol dicarboxylic acids and their derivatives are always used in comparison of the cast systems in humans, made possible by the first product offered [6]. Other diisocyanates and m-phenylenediamine are processable by hot cure systems. Crosslinking through the use of powdered crosslinkers. Many aromatic diisocyanates gives a special type of reactive diamine (MDA)₂ · NaCl, d